

Deposition of Ti:sapphire thin films by reactive pulsed laser ablation using liquid metals and oxygen

P. Manoravi¹, P.R. Willmott^{1,*}, J.R. Huber¹, T. Greber²

¹Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

²Physik Institut der Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Received: 21 July 1999/Accepted: 15 September 1999/Published online: 28 December 1999

Abstract. Ti:sapphire films were grown using molten Al–Ti alloy ablation targets with either O₂ gas pulses or O₂ background reactive medium on sapphire (0001) substrates. The films were characterized by the use of XRD, RHEED, AFM, and XPS. While the films deposited at a substrate temperature of 650 °C showed three-dimensional epitaxial growth, the films deposited at 1000 °C exhibited a two-dimensional structure. Annealing of the low-temperature deposited films improved the crystal quality but failed to improve the surface morphology. Ti exists in the host sapphire lattice in the form of Ti³⁺ for films deposited at lower temperatures, whereas it assumes the tetravalent form in the high-temperature deposited films. The valence states of Ti identified by XPS studies are in agreement with low-temperature luminescence results.

PACS: 42.70.Hj; 81.15.Fg; 82.80.Pv

Titanium doped sapphire is an important solid-state lasing medium, which in the form of a thin film could lead to the development of microlasers, waveguides, and optical amplifiers for application in optoelectronics and optical communications. Of the different techniques reported to date for depositing Ti:sapphire thin films, pulsed laser deposition (PLD) seems to be among the most promising [1, 2]. However, incorporation of macroscopic particulates originating from exfoliation of a solid ablation target in the growing film can undermine its quality. This well-known problem can be minimized by using a liquid target [3, 4]. In this paper, we report the deposition of Ti:sapphire thin films by PLD using a molten Al–Ti alloy target and an O₂ background or synchronized O₂ pulses as a reactive medium. The films were chemically analyzed by the use of X-ray photoelectron spectroscopy (XPS) for their Ti dopant concentration and valence state, while low-temperature luminescence measurements, shown elsewhere, were performed to determine the films' optical properties. X-ray diffraction (XRD), reflection high-energy

electron-diffraction (RHEED), and atomic force microscopy (AFM) were used to characterize the films' crystallographic and morphological properties.

1 Experimental

Details of the experimental setup are reported elsewhere [5, 6]. The molten target was prepared from a cylindrical Al slug (99.999% pure) and a small amount of Ti metal powder (> 98.5% pure), which were then heated to 750 °C. Ti dissolves in Al up to 0.17 at. % at 750 °C [7, 8]. The liquid was maintained at this temperature for 3 hours in order that the Al–Ti mixture could be homogenized prior to ablation. Deposition experiments were carried out using a KrF excimer laser (17 ns, 248 nm) at a fluence of 3 J cm⁻². The ablation plume was either crossed with synchronized O₂ (99.995% pure) pulses [5] of 400 μs width containing ~ 10¹⁷ molecules/pulse or expanded into a background of O₂ at a pressure between 2 × 10⁻² Pa and 7 Pa. Depositions were for 60 000 laser shots at 12 Hz on atomically polished sapphire (0001) substrates, located 40 mm from the target, at two different substrate temperatures (650 or 1000 °C). The thickness of the deposited films was determined by optical interference techniques and lay in the range 400 nm to 1 μm.

2 Results and discussion

There was no detectable difference between the films deposited using synchronized O₂ pulses and the background oxygen. The film crystallinity was examined by XRD and is summarized in Fig. 1. In addition to the (0006) substrate peak, XRD patterns of films grown at 650 °C showed a weak (0003) reflex, which is forbidden for pure sapphire. Such forbidden reflexes occur when the crystal symmetry is disturbed by substitutional and other types of defects. However, this reflex vanished after annealing of the low-temperature deposits at 1100 °C, and was not present for films grown at 1000 °C. XPS data showed that the Ti concentration was not affected by the growth temperature or annealing procedures (*vide infra*). Hence we conclude that the Ti impurity concentration is too small to offset the crystal symmetry and that the (0003)

*Corresponding author. (E-mail: willmott@pcizuse.unizh.ch)

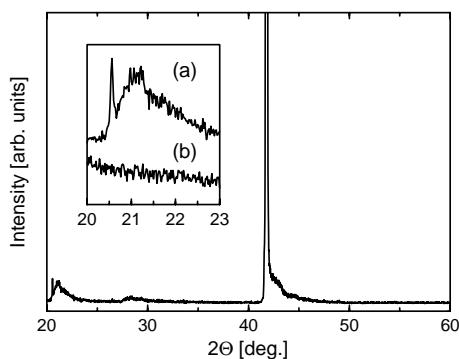


Fig. 1a,b. XRD spectrum of Ti:sapphire film deposited at a substrate temperature of 650 °C. The inset shows the forbidden sapphire (0003) peak for the as-deposited film (a), which vanishes after annealing at 1100 °C (b)

reflex in the low-temperature films is due to defects other than Ti substitution of the Al ions.

RHEED images were taken for films grown at the two substrate temperatures of 650 °C and 1000 °C; they are shown in Fig. 2. The films grown at the lower substrate temperature showed transmission electron diffraction images, indicative of three-dimensional epitaxy, while the high-temperature films maintained a two-dimensional Laue ring pattern.

Substrate temperatures in excess of 1000 °C are normally required to achieve good crystallinity in sapphire film growth [1, 2]. It is tentatively suggested that the reason we are able to grow crystalline films at relatively low temperatures is because our ablation target is metallic. The ablation yield of metals, especially those with the smallest absorption depths (such as Al at 248 nm), is lower than for ceramic targets, and much of the photonic energy is therefore channeled into heating the opaque nascent plasma by laser-supported absorption [9]. Hyperthermal species with kinetic energies of ~ 50 eV are thereby produced [10], and these promote surface mobility and crystalline growth as they impinge on the surface.

Figure 3 shows the surface morphology obtained by the use of AFM of Ti:sapphire films grown at different temperatures. The AFM picture of the sapphire (0001) substrate surface is shown in Fig. 3a for comparison. The film deposited at a substrate temperature of 650 °C shown in Fig. 3b has an average surface roughness (R_{av}) of 3.2 nm and a peak-to-valley (R_{pv}) roughness of 28.2 nm. Annealing this film at 1100 °C improved the crystallinity (*vide supra*), but did not change the surface morphology (Fig. 3c). However, Fig. 3d shows a smoother morphology for films deposited at 1000 °C: R_{av} and R_{pv} are 0.6 nm and 8 nm, respectively. Even though the latter film has a smoother surface with an average rough-

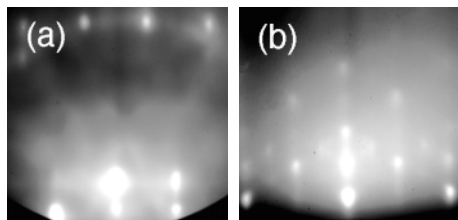


Fig. 2a,b. RHEED image of Ti:sapphire films grown at a 1000 °C, and b 650 °C. Note the two-dimensional Laue rings in a, while the pattern in b is typical of transmission electron diffraction of a three-dimensional structure

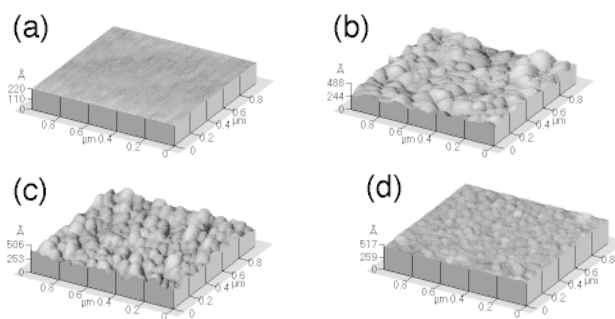


Fig. 3a–d. AFM images of a a sapphire (0001) substrate surface, b film grown at 650 °C, c film grown at 650 °C and annealed at 1100 °C, and d film grown at 1100 °C

ness of less than a unit cell, the other surfaces also have a roughness of only 2 to 3 unit cells. These results corroborate the findings by the use of RHEED.

The films were characterized using XPS. Monochromatic Al K_{α} (1486.6 eV) emission was used as the X-ray source at near-magic angle. In view of the very low Ti concentration in the films, the Ti 2*p* peaks were recorded with improved statistics. Figure 4 shows the overview XPS spectrum of a Ti:sapphire film deposited at 650 °C followed by annealing at 1100 °C with the inset showing the Ti 2*p* peaks. The concentration of Ti in the deposited films determined from XPS analysis was in the range 0.08 to 0.17 at. %.

Ti can exist in the sapphire host lattice as Ti^{3+} or Ti^{4+} ; the trivalent state is responsible for its broad-band luminescence between 650 and 950 nm. In order to determine the valence state of Ti in the film, Ti metal was deposited in situ by evaporation of a Ti filament in successive cycles involving submonolayer doses followed by XPS analysis, until the Ti 2*p* peak assumed the metallic position [11–13] and no further shift could be observed. Ti:sapphire is electrically insulating and hence the XPS peak positions are also influenced by charging effects. The chemical shift was therefore determined by additional measurement of the O 1*s* peak at each cycle so that calibration for shifts due to charging could be made. Figure 5 displays the Ti 2*p* peak positions recorded at different

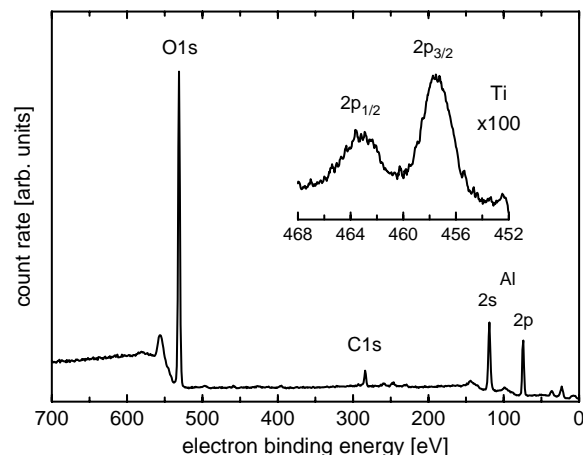


Fig. 4. XPS spectrum using Al K_{α} radiation of a Ti:sapphire film grown at 650 °C. The spectra have been adjusted for charging shifts. The C 1*s* signal could be assigned to surface adsorbates

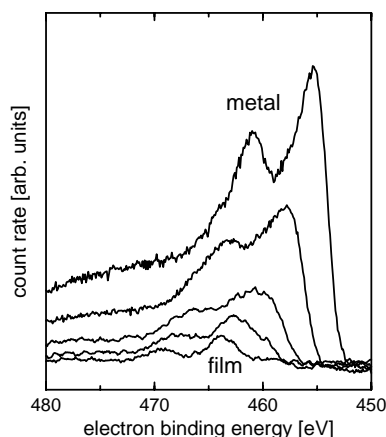


Fig. 5. XPS spectra of Ti 2p peaks at various stages of Ti metal deposition on the surface of the Ti:sapphire film

stages of surface Ti deposition. The shift in the Ti 2p peaks in the Ti:sapphire with respect to that of the metal is observed to be 4.37 eV for the films deposited at 1000 °C, similar to values found in the literature for the Ti^{4+} ion [11–13]. However, those films deposited at 650 °C showed a peak shifted by 3.4 eV, which corresponds to Ti^{3+} .

It was established that the position of the Ti^{3+} in the sapphire host lattice was identical to that of bulk Ti:sapphire by comparison of their low-temperature (10 K) luminescence spectra, shown elsewhere [6]. Films containing predominantly Ti^{4+} ions showed no luminescence, as expected [14]. The conditions needed to anneal under a reducing atmosphere and thereby avoid the oxidation of Ti^{3+} to Ti^{4+} have still to be established. It is expected, even under these conditions, that the luminescent properties will remain the same as those prior to annealing, for which no Ti^{4+} could be detected. Annealing might, however, reduce waveguide losses caused by scattering from grain boundaries.

3 Conclusions

Ti:sapphire films were successfully produced for the first time using molten Al–Ti ablation targets in either a pulsed or background oxidizing medium.

The valence state and therefore the optical properties of the Ti ion dopants depended on the deposition temperature, existing in the Ti^{3+} form in the low-temperature (650 °C) deposited films, but the tetravalent state for films grown at 1000 °C was assumed. No laser droplets could be found on the films, which were also very flat, with an average roughness of 3 monolayers or less even for those films grown at a substrate temperature of 650 °C. Annealing of the low-temperature films improved the crystal quality but failed to change the surface morphology.

Use of liquid metal alloys as the ablation target is a new technique which affords increased flexibility in the concentration and type of dopant in the growth of thin films of optically active materials, while being substantially more affordable than techniques that use bulk optical materials as the ablation target. Finally, it is speculated that because the ablation target differs from the film material, novel dopant-host thin film systems produced far from chemical equilibrium may become possible with this technique.

Acknowledgements. Support of this work by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung is gratefully acknowledged. Willi Auwärter is warmly thanked for his assistance in the AFM measurements.

References

1. A.A. Anderson, R.W. Eason, M. Jelinek, C. Grivas, D. Lane, K. Rogers, L.M.B. Hickey, C. Fotakis: *Thin Solid Films* **300**, 68 (1997);
2. A.A. Anderson, R.W. Eason, L.M.B. Hickey, M. Jelinek, C. Grivas, D.S. Gill, N.A. Vainos: *Opt. Lett.* **22**, 1556 (1997)
3. H. Sankur, W.J. Gunning, J. DeNatale, J.F. Flintoff: *J. Appl. Phys.* **65**, 2475 (1989)
4. P.R. Willmott, F. Antoni: *Appl. Phys. Lett.* **73**, 1394 (1998)
5. P.R. Willmott, R. Timm, J.R. Huber: *J. Appl. Phys.* **82**, 2082 (1997)
6. P.R. Willmott, P. Manoravi, J.R. Huber, T. Greber, K. Holliday, T. Murray: *Opt. Lett.* **24**, 1581 (1999)
7. J.L. Murray, A.J. McAlister, *Binary Alloy Phase Diagrams*, Vol. I, ed. by T.B. Massalski (The American Society of Metals 1986)
8. J.L. Murray: *Metall. Trans. A* **19**, 243 (1988)
9. R.W. Dreyfus: *J. Appl. Phys.* **69**, 1721 (1991)
10. R. Timm, P.R. Willmott, J.R. Huber: *J. Appl. Phys.* **80**, 1794 (1996)
11. C. Oviedo: *J. Phys.: Condens. Matter* **5**, A153 (1993)
12. J.T. Mayer, U. Diebold, T.E. Madey, E. Garfunkel, J. Electron. Spectrosc. Relat. Phenom. **73**, 1 (1995)
13. H. Idriss, K.S. Kim, M.A. Barteau: *Surf. Sci.* **262**, 113 (1992)
14. T.S. Bessonova, M.P. Stanislavskii, V.Ya. Khaimov-Malkov: *Opt. Spectrosc.* **41**, 87 (1976)